

# **Immediate Action Levels for Water Treatment Plant Chemicals**

**Massachusetts Department of Environmental Protection  
Office of Research and Standards  
1 Winter Street  
Boston, MA 02108 USA**

**April 2008**

### **Immediate Action Levels for Water Treatment Plant Chemicals**

In response to a number of incidents at treatment plants for public water supplies resulting in the need for emergency measures to be taken, MassDEP has derived Immediate Action Levels for a number of indicator parameters for commonly used treatment chemicals. These limits are intended for use by plant operators to identify when a situation involving chemical over-feeds or use of the wrong chemical has occurred of sufficient gravity to require the implementation of emergency response procedures. These parameters are frequently and routinely monitored in the treatment plant. In addition to the levels listed below, water delivered to the entry point of the distribution system is also required to meet various other federal and state standards and guidelines (see listing at: <http://www.mass.gov/dep/water/laws/regulati.htm#chems>).

#### **Immediate Action Levels for Water Treatment Plant Chemicals**

<b>Indicator Treatment Chemical</b>	<b>Immediate Action Level</b>
High pH	pH levels > 11
Low pH	pH levels < 4.5
Fluoride	10 mg/L
Free chlorine	25 mg/L
Chlorine dioxide	<i>under development</i>

The following information describes the bases for these values.

#### **I. Recommended pH Guidelines**

**A pH value of 11 is recommended as an upper do not use/do not drink value. Solutions with pH values at or above this value, lacking other information on the factors noted below, should be considered to present a significant risk of skin and eye irritation and possible exacerbation of skin disorders. In order to avoid potential ocular irritant effects and reversible damage, water with a pH of below 4.5 should not be used.**

pH is a measure of the effective concentration of hydrogen ions and is expressed on a scale that ranges from 0-14 units. Because it uses a log scale, a change of one pH unit corresponds to a change in the hydrogen ion concentration of a factor of 10. USEPA recommends that drinking waters be maintained at pH values between 6.5 and 8.5 to avoid adverse aesthetic impacts. Adjustments to somewhat higher pH's (e.g. up to 9) are sometimes used to minimize leaching of metals, in particular lead, into drinking water from pipes within the distribution system.

Strong acids typically cause tissue damage by denaturing proteins. Strong bases can both denature proteins and saponify fats, which facilitates tissue penetration and damage. Effects may range from mild irritation to severe burns. The likelihood and severity of effect depends on the pH; the buffering capacity of the water; the amount or volume of exposure; the duration and frequency of exposure; and individual sensitivity.

## High pH

Water with significantly elevated pH values can irritate, and at high enough values, severely damage mucus membranes, the eye, throat and skin if consumed or used for washing. Elevated pH can also cause the water to feel slippery and taste alkali (bitter), make it difficult to get soaps and detergents to lather, and lead to the formation of precipitate deposits in pipes and on clothing and dishes. Elevated pH water could also impact the effectiveness of certain medicines.

According the World Health Organization eye irritation and exacerbation of skin disorders have been associated with exposures to water with pH values greater than 11 (WHO, 1996). Solutions with pH values of 12.5 or greater have been reported to cause significant tissue damage including esophageal ulceration when consumed. Such effects can be serious and of longer duration and would warrant immediate medical evaluation.

## Low pH

Under the Safe Drinking Water Act the lower limit secondary maximum contaminant level for pH was established at 6.5. This value was selected to minimize the corrosivity of drinking water in the distribution system and thus minimize leaching of lead, cadmium, copper, iron, and zinc from metal pipes and the mobilization of asbestos from corrosion of cement asbestos pipes.

Although many foods, including lemon juice and carbonated beverages may have pH values as low as 2.5, Potts (1991) reports that “as the pH of buffered solutions applied to the human eye is decreased from 7.4, the onset of discomfort begins at about pH 4.5. Between pH 4.5 and 3.5, one creates punctate breaks in the corneal epithelium that are stainable with fluorescein but heal in a few hours’ time.”

Thus, to avoid the potential for ocular irritant effects and reversible damage it is recommended that water with a pH below 4.5 not be used.

## II. Recommended Fluoride Guideline

**A fluoride value of 10 mg/L is recommended as a do not drink or use limit.**

Concentrations below 10 mg/L are protective of potential nausea, vomiting and gastric pain that may occur at higher values. A fluoride value of <10 mg/L is recommended to also protect against skin rashes and itching that may occur as a result of dermal contact with the water.

The acute health effects of fluoride may include severe nausea, vomiting, excess saliva production, abdominal pain and diarrhea. More serious acute health effects are convulsions, irregular heartbeat and coma. After being ingested into the stomach, 50% of sodium fluoride is typically converted into hydrofluoric acid (HF), which is absorbed through the mucous membrane of the stomach at a rate 1,000,000 times greater than F<sup>-</sup>.

Fluoride then circulates in the body and returns to the mouth through the salivary glands. HF formation in the stomach is pH dependent, with more being formed at lower pH values. The U.S. Center for Disease Control (CDC 1995) has recommended that, if the fluoride level in a community water system exceeds 10 mg/L, the fluoridation system be turned off immediately in order to protect public health. At 10 mg F/L, it is estimated that a 2 year old, weighing 10 kilograms and drinking one liter of water would receive a fluoride dose that is associated with gastrointestinal symptoms, requiring treatment. At higher levels more severe health effects would occur.

Infants (ages birth to 12 months) who are fed reconstituted infant formula mixed with tap water as a primary source of nutrition represent a high risk group, mainly due to their higher ingestion rate per smaller unit of body weights. The American Dental Association recommends the use of fluoride-free water for mixing formula. Infants and young children are also more susceptible to the effects of fluoride on the thyroid gland (endocrine disruption) and to dental fluorosis (NRC, 2006).

There is little information about the effects of fluoride from non-drinking water exposures. One community health study reported that skin contact with 50 mg/L fluoride caused itching and skin rashes (Petersen et al., 1988). No other studies on the water concentration of fluoride and dermal effects were found.

10 mg F/L of water is recommended as a do not use value for the following reasons:

- 50 mg/L fluoride is a frank effect level and dermal effects at lower concentrations, including 10 mg/L, cannot be ruled out;
- If water at concentrations higher than 10 mg F/L is available to the public, its likely that people may accidentally drink the water and become ill; and,
- Selecting 10 mg F/L as a do not drink or use value will be easier to communicate and will minimize confusion and/or mishaps compared to having multiple values for consumptions versus other uses.

The U.S. Environmental Protection Agency (US EPA 1986) has set an enforceable drinking water standard for fluoride of 4 mg/L (some people who drink water containing fluoride in excess of this level over many years could get bone disease, including pain and tenderness of the bones). EPA has also set a secondary fluoride standard of 2 mg/L to protect against dental fluorosis. Dental fluorosis, in its moderate or severe forms, may result in a brown staining and/or pitting of the permanent teeth. This problem occurs only in developing teeth, before they erupt from the gums. Children under nine should not drink water that has more than 2 mg/L of fluoride on a long-term basis. The EPA MCL of 4.0 mg/L is based on chronic effects and risk balancing. The Secondary MCL of 2.0 mg/L has been set to protect against dental fluorosis.

### **III. Recommended Limits for Free Chlorine for the Disinfectants Chlorine and Chloramines**

**A free chlorine concentration of 25 mg/L should be used as an emergency acute effects level for water treatment facilities employing chlorine or chloramines as disinfectants.**

Facilities which treat with the oxidants chlorine or monochloramine monitor in real- or near real-time the amount of total and or free or residual chlorine in the water that they treat. Assuming that there is no continuous monitoring for the concentrations of the second or third added oxidants themselves, an acute exposure limit for chlorine only will be identified to be used with facilities that employ these different disinfectants.

The U.S. Environmental Protection Agency's Drinking Water Criteria Document for Chlorine (US EPA 1994) summarizes the health effects of exposure to chlorine which is a strong respiratory and dermal irritant.

There is a federal standard of 4 mg/L for chlorine in drinking water known as a Maximum Residual Disinfectant Level (MRDL). An MRDL is "a level of a disinfectant added for water treatment that may not be exceeded at the consumer's tap without an unacceptable possibility of adverse health effects. For chlorine and chloramines, a PWS is in compliance with the MRDL when the running annual average of monthly averages of samples taken in the distribution system, computed quarterly, is less than or equal to the MRDL. MRDLs are enforceable in the same manner as maximum contaminant levels under Section 1412 of the Safe Drinking Water Act. Notwithstanding the MRDLs, operators may increase residual disinfectant levels of chlorine or chloramines (but not chlorine dioxide) in the distribution system to a level and for a time necessary to protect public health to address specific microbiological contamination problems caused by circumstances such as distribution line breaks, storm runoff events, source water contamination, or cross-connections." (US EPA 2000). Since compliance is based on an annual average, the MRDL does not apply to individual samples that are allowed to be higher than the MRDL (US EPA 1994). Because of the manner of derivation of the MRDLs and the fact that they can be exceeded in drinking water treatment systems, they do not appear as appropriate values to use as a cutoff value requiring issuance of "Do Not Drink" or "Do Not Bathe" notices during upset conditions.

The MRDL was set using toxicological data from a chronic rat study. The value was derived to be protective of human health with chronic exposure and includes uncertainty factors. It therefore is not the sort of number that could serve as an emergency level from a toxicological point of view. During an upset emergency, exposures would be of short-term or acute duration. From an operational perspective it seems best to have a limit representing conditions where adverse effects would be expected if exposures took place.

The US EPA identifies Health Advisory values for short-term exposures to chemicals. They did not find suitable information for determining a One-day Health Advisory (HA) for chlorine. They did find suitable data to allow them to derive a 10-day HA value of 3 mg/L (US EPA 2006). EPA notes that in the absence of a unique 1-day value, the 10-day value is a conservative estimate for a 1-day exposure. The values do not appear to be

appropriate for use as an acute shutdown or “Do Not Drink” level because they are based on an animal no adverse effects level (NOAEL) which was numerically reduced by the application of a total of 100-fold of uncertainty factors applied for interspecies extrapolation and recognition of the variation in sensitivity across the population. Temporary exceedance of the 1-day value would not necessarily reflect a critical enough situation to warrant shutting down a water system or issuing use limitation notices. However, the information on which the HA is based can serve as a basis for identifying an acute exposure limit not to be exceeded. The current 10-day HA value is based upon a NOAEL (25 mg/kg/d or 200 mg/L) from a mouse study by (Blabau and Nichols 1956). There was an absence of gross lesions, histological abnormalities and changes in weight or growth over the 50-day exposure period. Ideally, an acute limit for use at a treatment plant should be near an effect level for a chemical. In order to translate the NOAEL used for the 10-day HA value into an effect level, it can be multiplied by a factor of 10 to reflect the standard conversion factor used when extrapolating lowest adverse effect levels (LOAELs) to NOAELS (in those cases dividing by the factor of 10 to reduce the LOAEL dose to a NOAEL dose). The LOAEL values can then be numerically decreased by dividing by 10 and 10 for interspecies extrapolation and sensitivity in the population. The resulting drinking water concentration for a child (assumed 10 kg body weight ingesting 1L of water per day) would be **25 mg/L**. This value is graphically contrasted against other reported effects levels from the literature to put it in perspective.

This concentration should also be used to indicate the likely potential for dermal and ocular irritation through uses of the drinking water in the home for bathing or showering, although no dose-response information for these types of acute exposures has been located. Operational guidance for the treatment of swimming pools and whirlpool baths may provide some perspective. Recommended free chlorine concentrations in properly maintained swimming pools disinfected with chlorine (in several different forms) range from 1.5 – 2.0 mg/L. The Centers for Disease Control’s recommended levels in spas and whirlpool baths are >3 - <10 mg/L. The degree of ocular irritation is also a function of the chlorine species present and the pH level, with the potential for irritation being more pronounced at lower pHs.

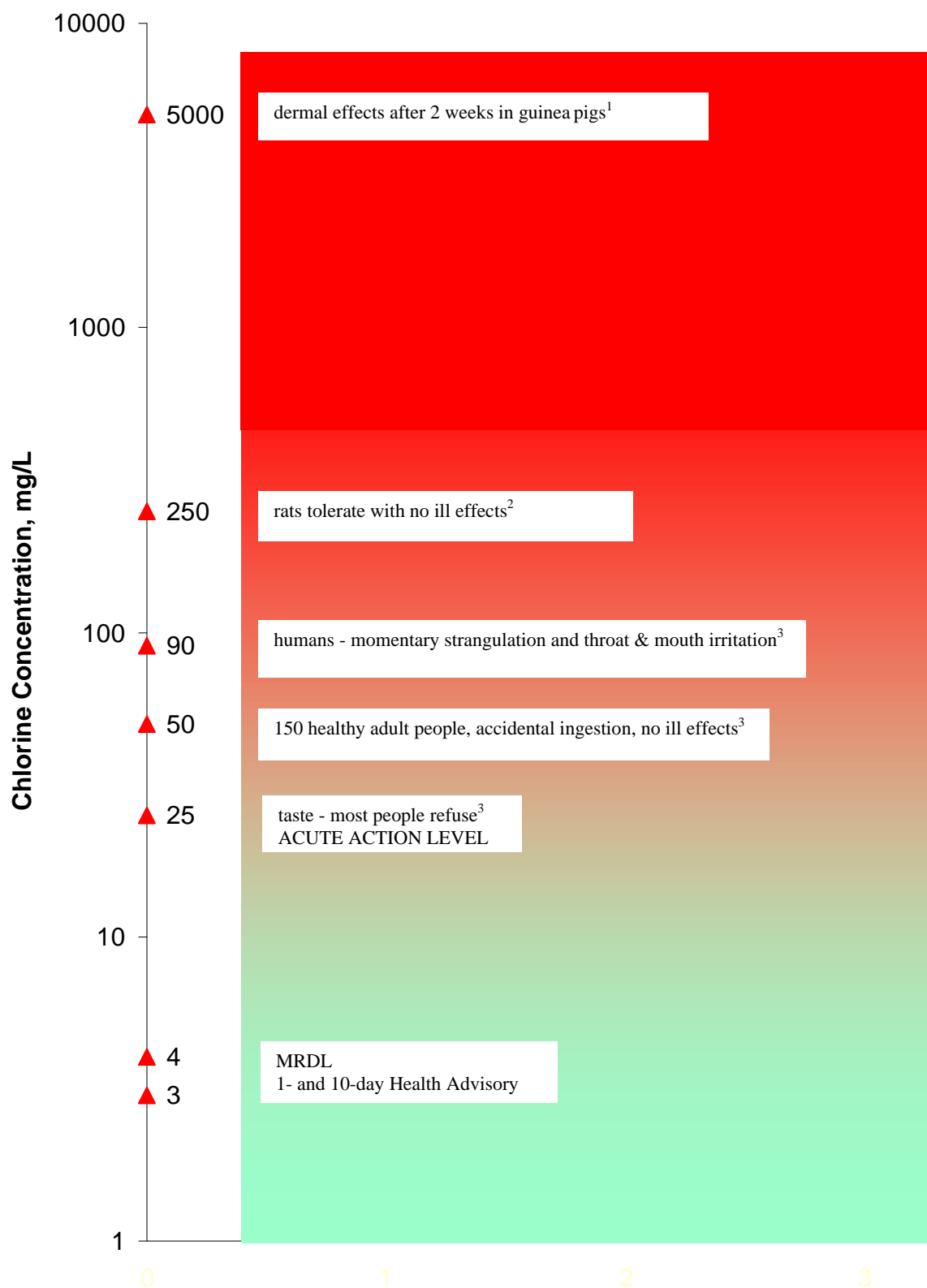


Figure 1. Chlorine Effects Levels, Exposure Limits and Recommended Acute Emergency Level for Drinking Water Treatment Plants. <sup>1</sup>- Cotter et al., 1985; <sup>2</sup>- Druckrey 1968, Furukawa et al 1980, Hasegawa et al 1986 and Kurokawa et al. 1986b cited in Bull 1992; <sup>3</sup>- Muegge et al. 1956 cited n US EPA 1995; <sup>4</sup>- FR. 1994. Drinking Water; National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts. U.S. Environmental Protection Agency. 40 CFR Parts 141 and 142. Para IX. D.July 29, 1994. 38668-38829.

#### **IV. Recommended Limits for the Disinfectant Chlorine Dioxide**

##### **Recommendation under development**

#### **REFERENCES**

Blabaum, D.J. and Nichols, M.S. (1956). Effect of highly chlorinated water on white mice. *J. Am. Water Works Assoc.* 4, 1503-1506

Bull R.J. (1992). Drinking Water Disinfection. p 267-318. In, M. Lippmann, ed. *Environmental Toxicants: Human Exposures and Their Health*. 1st ed. John Wiley & Sons.

CDC (1995). Engineering and Administrative Recommendations for Water Fluoridation. *Morbidity and Mortality Weekly Report*, September 29, 1995;44(RR-13):1-40

Cotter J.L., Fader R.C., Lilley C., Herndon D.N. (1985). Chemical parameters, antimicrobial activities, and tissue toxicity of 0.1 and 0.5% sodium hypochlorite solutions. *Antimicrob Agents Chemother* 28(1):118-22.

Muegge O.J. (1956). Physiological effects of heavily chlorinated drinking water. *Journal American Water Works Association* 48:1507-9.

NRC (2006). Fluoride in Drinking Water: A Scientific Review of EPA's Standards. National Research Council. National Academies Press. Washington, DC.

Petersen et al. (1988). Community health effects of a municipal water system hyperfluoridation accident. *American Journal of Public Health*. 78(6): 711-713.

Potts, A.M. (1991). *Toxic Responses of the Eye*, In, Amdur MO, Doull J, Klaassen CD. (eds.) 1991. Casarett and Doull's Toxicology. The Basic Science of Poisons Volume. 4th. New York: Pergamon Press.

US EPA (1986) National Primary And Secondary Drinking Water Regulations: Fluoride, Final Rule. *Federal Register* April 2, 1986.

US EPA (1994) Drinking Water; National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts. U.S. Environmental Protection Agency. 40CFR Parts 141 and 142. Para IX. D. FR July 29, 1994. 38668-38829.

US EPA (1995). Draft Chlorine Drinking Water Health Advisory. Office of Water. Washington, DC.

US EPA (2000) Definition of MRDL. 40 CFR 141.2: Subpart A-General, Definitions.

US EPA (2006) 2006 Edition of the Drinking Water Standards and Health Advisories. EPA 822-R-06-013. Office of Water. Washington, DC. Available online at:  
<http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf>

World Health Organization (WHO), Background Document for Development of WHO Guidelines for Drinking-water Quality (1996)  
[http://www.who.int/water\\_sanitation\\_health/dwq/chemicals/en/ph.pdf](http://www.who.int/water_sanitation_health/dwq/chemicals/en/ph.pdf)